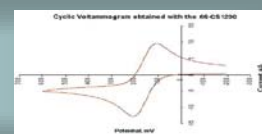


## Analytical Electrochemistry: The Basic Concepts



### c) Anodic Stripping Voltammetry.

Anodic stripping voltammetry (ASV) is the most common of a class of techniques known as *stripping electroanalytical methods (SEAM)*. The defining characteristic of these methods is the *preconcentration of analyte* at the electrode surface in order to lower the detection limit for that analyte.<sup>15</sup> ASV involves the accumulation of electroactive material at the electrode by the application of a potential well negative of its  $E^0$  value. Usually a mercury drop or mercury thin-film electrode is employed under forced convective conditions (stirred solution). The preconcentration step is followed by a short time period in which the solution is allowed to quiet (no stirring), following which a potential scan is initiated from the deposition potential in the anodic direction.

ASV is well-suited for the determination of trace amounts of many metal contaminants. “Stripping” refers to the characteristic sharp voltammetric waves that occur for metals as they are oxidized out of mercury, in which many metals form amalgams. Approximately a dozen metals can be conveniently analyzed using ASV, with more than a dozen more elements amenable to analysis with slight modification of the basic technique.<sup>16</sup>

The concentration of the reduced metal following the deposition step is generally 100 – 1000 times the original solution concentration. Deposition times range from *ca.* 30 seconds for solutions containing metal ions at concentrations on the order of  $10^{-7}$  M up to more than 20 minutes for those down to  $10^{-10}$  to  $10^{-11}$  M.<sup>17</sup> Standard solutions containing known quantities of each analyte are used to calibrate the stripping response. The current magnitude (peak height) or charge (peak area) of the anodic wave may be used to quantify unknown amounts of analyte. Experimental conditions, such as rate of stirring and deposition time must be carefully controlled to assure reproducibility of results.

Most commonly, a linear potential sweep is used for anodic stripping. Peak potentials are characteristic of each analyte, and frequently multiple metals can be analyzed in a single measurement. The stripping peak current observed at a hanging mercury drop electrode (HMDE) is given (at 25 °C) by

$$i_p = 2.72 \times 10^5 n^{3/2} A D^{1/2} v^{1/2} C_M$$

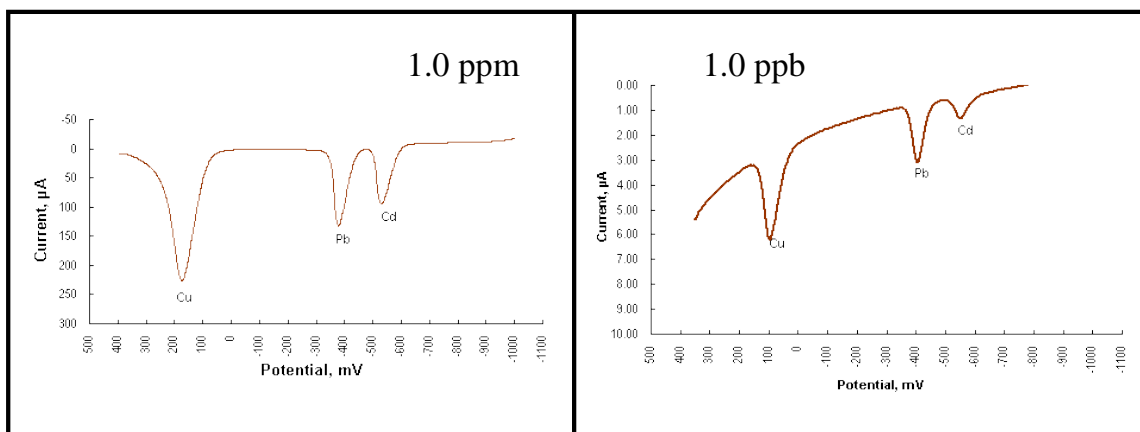
where  $n$  = number of electrons involved in the oxidation,  $A$  is the electrode area in  $\text{cm}^2$ ,  $D$  is the diffusion coefficient for the metal within the mercury drop expressed in  $\text{cm}^2/\text{s}$ ,  $v$  is the scan rate in  $\text{V/s}$ , and  $C_M$  is the concentration of the metal within the mercury drop given as  $\text{mol/cm}^3$ . For a mercury film deposited on the surface of an inert substrate (like C or noble metal), the stripping peak current is given by

$$i_p = \frac{n^2 F^2 v^{1/2} A I C_M}{2.7 R T}$$

where  $F$  is the Faraday ( $9.65 \times 10^4$  C),  $I$  is the mercury film thickness in cm, and other symbols are as defined previously.

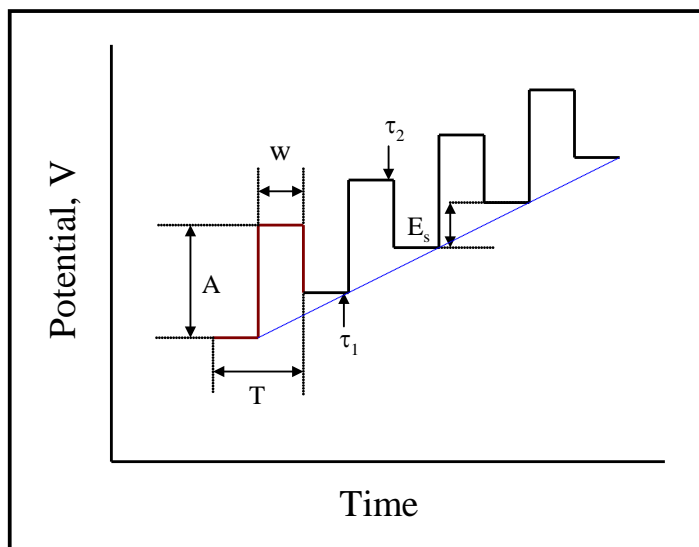
Typical results for the ASV analysis of Cd, Pb, and Cu contained in 0.10 M  $\text{KNO}_3$ /5%  $\text{HNO}_3$  electrolyte at a concentration of 1.0 ppm and 1.0 ppb are shown in shown **Figure 30** ([www.cypresssystems.com/Experiments/asv.html](http://www.cypresssystems.com/Experiments/asv.html)).<sup>18</sup> A thin mercury film was formed at the surface of a 1 mm glassy carbon electrode during the deposition step from mercuric nitrate added to the cell at a concentration of 30 ppm. The deposition step was 130 seconds, with the solution being stirred for the first 120 seconds. The scan rate was 1000 mV/s.

**Figure 30**



Improved detection limits are possible in ASV when using potential waveforms other than the linear sweep described above. Most are “step” methods that take advantage of the fact that the capacitive (background) component of the total current observed following a potential step decays more quickly (as  $t^{-1}$ ) than does the faradaic component (as  $t^{-1/2}$ ). One such technique, differential pulse voltammetry (DPV), uses a *staircase* potential waveform superimposed on the top of the linear (DC) waveform of LSV. The waveform is illustrated in **Figure 31**.

**Figure 31**



In DPV, the current is sampled at two points during a potential pulse of duration  $T$ . The first current measurement is made at some time  $\tau_1$  prior to the forward step of potential amplitude  $A$ , whose duration is designated  $W$ . The second current measurement is made at a similar time period following the potential step, at  $\tau_2$ . The potential is then stepped back to a point on the DC ramp (blue dotted line)  $E_s$  volts higher than the previous step. The difference between the two currents is plotted as a function of the applied DC potential. Using this method, the non-faradaic component of the current is largely removed, and the signal-to-noise ratio is enhanced. More information on DPP and other pulse techniques can be found at <http://www.epsilon-web.net/Ec/manual/Techniques/Pulse/pulse.html>.<sup>19</sup>

Cathodic stripping analysis (CSV) involves an anodic deposition step followed by a potential scan in the cathodic direction. Applications of CSV include many organic and inorganic compounds, and anions, which form insoluble salts with mercury.<sup>20</sup>